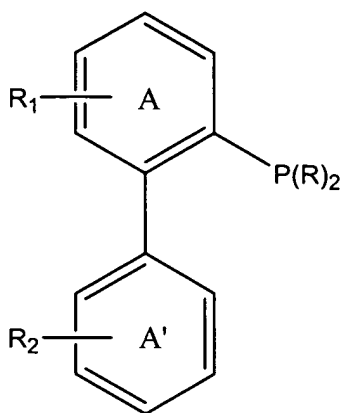


We claim:

1. A ligand represented by structure I:



I

wherein

R is selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and $-(CH_2)_m-R_{80}$;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R₁ and R₂, respectively, any number of times up to the limitations imposed by stability and the rules of valence;

R₁ and R₂, when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, $-SiR_3$, and $-(CH_2)_m-R_{80}$;

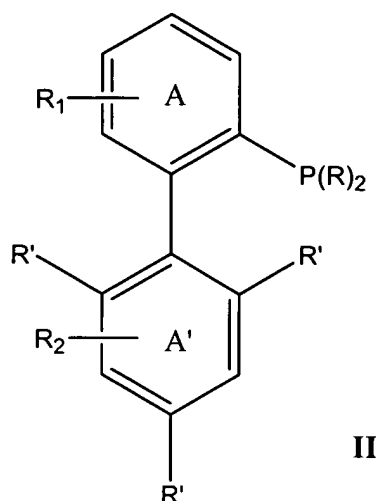
R₈₀ represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer.

2. The ligand of claim 1, wherein R represents independently for each occurrence alkyl, cycloalkyl or aryl; at least two instances of R₂ are present; and R₂ is selected independently for each occurrence from the group consisting of alkyl and cycloalkyl.

3. A ligand represented by structure II:



wherein

R and R' are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, and $-(CH_2)_m-R_{80}$;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R_1 and R_2 , respectively, any number of times up to the limitations imposed by stability and the rules of valence;

R_1 and R_2 , when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, halogen, $-SiR_3$, and $-(CH_2)_m-R_{80}$;

R_{80} represents independently for each occurrence cycloalkyl or aryl;

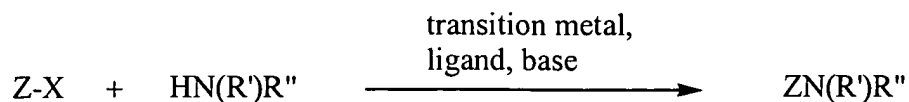
m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer.

4. The ligand of claim 3, wherein R_1 is absent; and R_2 is absent.
5. The ligand of claim 3, wherein R represents independently for each occurrence alkyl or cycloalkyl.
6. The ligand of claim 3, wherein R represents independently for each occurrence ethyl, cyclohexyl, cyclopropyl, isopropyl or *tert*-butyl.
7. The ligand of claim 3, wherein R represents independently for each occurrence

cyclohexyl.

8. The ligand of claim 3, wherein R' represents independently for each occurrence alkyl.
9. The ligand of claim 3, wherein R' represents independently for each occurrence isopropyl.
10. The ligand of claim 3, wherein R₁ is absent; R₂ is absent; and R represents independently for each occurrence alkyl or cycloalkyl.
11. The ligand of claim 3, wherein R₁ is absent; R₂ is absent; and R represents independently for each occurrence ethyl, cyclohexyl, cyclopropyl, isopropyl or *tert*-butyl.
12. The ligand of claim 3, wherein R₁ is absent; R₂ is absent; and R represents independently for each occurrence cyclohexyl.
13. The ligand of claim 3, wherein R₁ is absent; R₂ is absent; R represents independently for each occurrence alkyl or cycloalkyl; and R' represents independently for each occurrence alkyl.
14. The ligand of claim 3, wherein R₁ is absent; R₂ is absent; R represents independently for each occurrence ethyl, cyclohexyl, cyclopropyl, isopropyl or *tert*-butyl; and R' represents independently for each occurrence alkyl.
15. The ligand of claim 3, wherein R₁ is absent; R₂ is absent; R represents independently for each occurrence cyclohexyl; and R' represents independently for each occurrence alkyl.
16. The ligand of claim 3, wherein R₁ is absent; R₂ is absent; R represents independently for each occurrence alkyl or cycloalkyl; and R' represents independently for each occurrence isopropyl.
17. The ligand of claim 3, wherein R₁ is absent; R₂ is absent; R represents independently for each occurrence ethyl, cyclohexyl, cyclopropyl, isopropyl or *tert*-butyl; and R' represents independently for each occurrence isopropyl.
18. The ligand of claim 3, wherein R₁ is absent; R₂ is absent; R represents independently for each occurrence cyclohexyl; and R' represents independently for each occurrence isopropyl.
19. A method represented by Scheme 1:



Scheme 1

wherein

Z is selected from the group consisting of optionally substituted aryl, heteroaryl and alkenyl;

X is selected from the group consisting of Cl, Br, I, -OS(O)₂alkyl, and -OS(O)₂aryl;

R' and R'' are selected, independently for each occurrence, from the group consisting of H, alkyl, heteroalkyl, aryl, formyl, acyl, alkoxycarbonyl, alkylaminocarbonyl, heteroaryl, aralkyl, alkoxyl, amino, trialkylsilyl, and triarylsilyl;

R' and R'', taken together, may form an optionally substituted ring consisting of 3-10 backbone atoms inclusive; said ring optionally comprising one or more heteroatoms beyond the nitrogen to which R' and R'' are bonded;

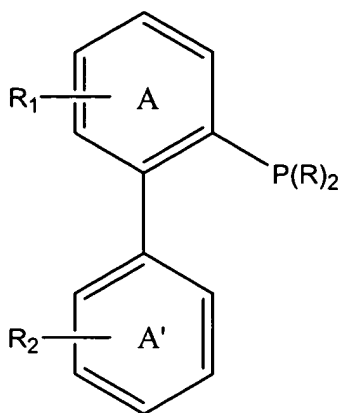
R' and/or R'' may be covalently linked to Z;

the transition metal is selected from the Group 10 metals;

the base is selected from the group consisting of fluorides, hydrides, hydroxides, carbonates, phosphates, alkoxides, metal amides, and carbanions; and

the ligand is selected from the group consisting of:

compounds represented by I:



wherein

R is selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and $-(CH_2)_m-R_{80}$;

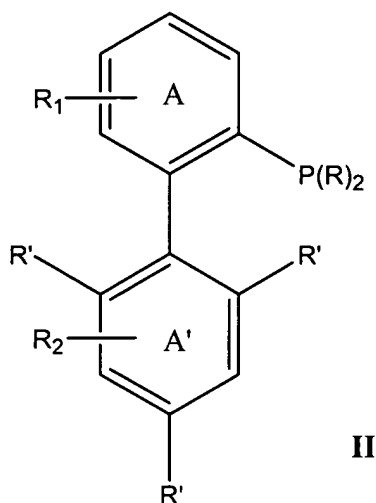
the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R_1 and R_2 , respectively, any number of times up to the limitations imposed by stability and the rules of valence;

R_1 and R_2 , when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, $-SiR_3$, and $-(CH_2)_m-R_{80}$;

R_{80} represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer; and
compounds represented by **II**:



wherein

R and R' are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, and $-(CH_2)_m-R_{80}$;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R₁ and R₂, respectively, any number of times up to the limitations imposed by stability and the rules of valence;

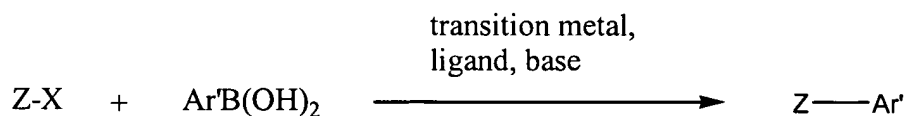
R₁ and R₂, when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, halogen, $-SiR_3$, and $-(CH_2)_m-R_{80}$;

R₈₀ represents independently for each occurrence cycloalkyl or aryl;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer.

20. The method of claim 19, wherein the transition metal is palladium.
21. The method of claim 19, wherein Z represents optionally substituted aryl.
22. A method represented by Scheme 2:



Scheme 2

wherein

Z and Ar' are independently selected from the group consisting of optionally substituted aryl, heteroaryl and alkenyl;

X is selected from the group consisting of Cl, Br, I, -OS(O)₂alkyl, and -OS(O)₂aryl;

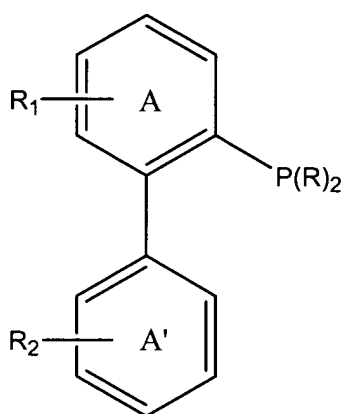
Z and Ar' may be covalently linked;

the transition metal is selected from the Group 10 metals;

the base is selected from the group consisting of fluorides, hydrides, hydroxides, carbonates, phosphates, alkoxides, metal amides, and carbanions; and

the ligand is selected from the group consisting of:

compounds represented by I:



I

wherein

R is selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and -(CH₂)_m-R₈₀;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R₁ and R₂, respectively, any number of times up to the limitations imposed by stability and the rules of valence;

R₁ and R₂, when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, -SiR₃,

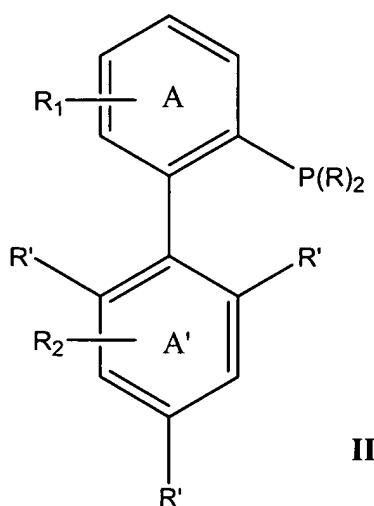
and $-(CH_2)_m-R_{80}$;

R_{80} represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer; and

compounds represented by **II**:



wherein

R and R' are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, and $-(CH_2)_m-R_{80}$;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R_1 and R_2 , respectively, any number of times up to the limitations imposed by stability and the rules of valence;

R_1 and R_2 , when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, halogen, $-SiR_3$, and $-(CH_2)_m-R_{80}$;

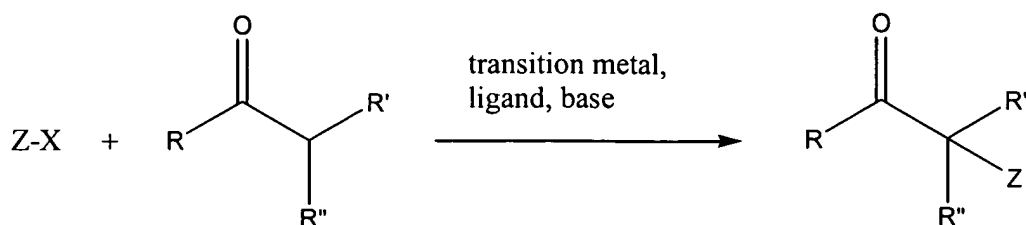
R_{80} represents independently for each occurrence cycloalkyl or aryl;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer.

23. The method of claim 22, wherein the transition metal is palladium.

24. The method of claim 22, wherein Z represents optionally substituted aryl.
25. The method of claim 22, wherein X is $-\text{OS}(\text{O})_2\text{aryl}$.
26. The method of claim 22, wherein X is $-\text{OS}(\text{O})_2\text{tolyl}$ or $-\text{OS}(\text{O})_2\text{phenyl}$.
27. The method of claim 22, wherein X is $-\text{OS}(\text{O})_2\text{tolyl}$.
28. The method of claim 22, wherein the base is selected from the group consisting of fluorides, carbonates, and phosphates.
29. The method of claim 22, wherein the base is cesium fluoride, potassium fluoride, cesium carbonate, or potassium phosphate.
30. The method of claim 22, wherein the transition metal is palladium; and X is $-\text{OS}(\text{O})_2\text{aryl}$.
31. The method of claim 22, wherein the transition metal is palladium; and X is $-\text{OS}(\text{O})_2\text{tolyl}$ or $-\text{OS}(\text{O})_2\text{phenyl}$.
32. The method of claim 22, wherein the transition metal is palladium; and X is $-\text{OS}(\text{O})_2\text{tolyl}$.
33. The method of claim 22, wherein the transition metal is palladium; X is $-\text{OS}(\text{O})_2\text{aryl}$; and the base is selected from the group consisting of fluorides, carbonates, and phosphates.
34. The method of claim 22, wherein the transition metal is palladium; X is $-\text{OS}(\text{O})_2\text{tolyl}$ or $-\text{OS}(\text{O})_2\text{phenyl}$; and the base is selected from the group consisting of fluorides, carbonates, and phosphates.
35. The method of claim 22, wherein the transition metal is palladium; X is $-\text{OS}(\text{O})_2\text{tolyl}$; and the base is selected from the group consisting of fluorides, carbonates, and phosphates.
36. The method of claim 22, wherein the transition metal is palladium; X is $-\text{OS}(\text{O})_2\text{aryl}$; and the base is cesium fluoride, potassium fluoride, cesium carbonate, or potassium phosphate.
37. The method of claim 22, wherein the transition metal is palladium; X is $-\text{OS}(\text{O})_2\text{tolyl}$ or $-\text{OS}(\text{O})_2\text{phenyl}$; and the base is cesium fluoride, potassium fluoride, cesium carbonate, or potassium phosphate.
38. The method of claim 22, wherein the transition metal is palladium; X is $-\text{OS}(\text{O})_2\text{tolyl}$; and the base is cesium fluoride, potassium fluoride, cesium carbonate, or potassium phosphate.
39. A method represented by Scheme 3:



Scheme 3

wherein

Z is selected from the group consisting of optionally substituted aryl, heteroaryl, and alkenyl;

R is selected from the group consisting of H, alkyl, heteroalkyl, aralkyl, aryl, heteroaryl, alkoxyl, alkylthio, alkylamino, and arylamino;

R' is selected from the group consisting of H, alkyl, heteroalkyl, aralkyl, aryl, heteroaryl, formyl, acyl, alkoxycarbonyl, alkylaminocarbonyl, and arylaminocarbonyl;

R'' is selected from the group consisting of H, alkyl, heteroalkyl, aralkyl, aryl, and heteroaryl;

X is selected from the group consisting of Cl, Br, I, -OS(O)₂alkyl, and -OS(O)₂aryl;

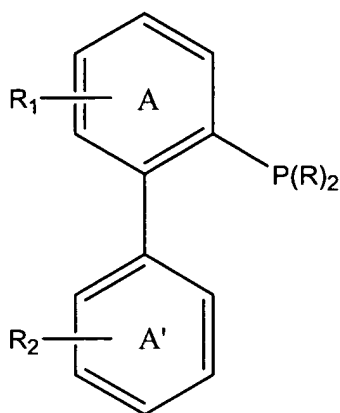
Z and one of R, R', and R'' may be covalently linked;

the transition metal is selected from the Group 10 metals;

the base is selected from the group consisting of fluorides, hydrides, hydroxides, carbonates, phosphates, alkoxides, metal amides, and carbanions; and

the ligand is selected from the group consisting of:

compounds represented by I:



I

wherein

R is selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and $-(CH_2)_m-R_{80}$;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R_1 and R_2 , respectively, any number of times up to the limitations imposed by stability and the rules of valence;

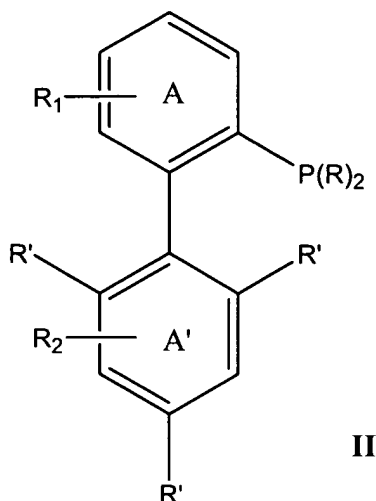
R_1 and R_2 , when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, $-SiR_3$, and $-(CH_2)_m-R_{80}$;

R_{80} represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer; and

compounds represented by **II**:



wherein

R and R' are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, and $-(CH_2)_m-R_{80}$;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R_1 and R_2 , respectively, any number of times up to the limitations imposed by stability and the rules of valence;

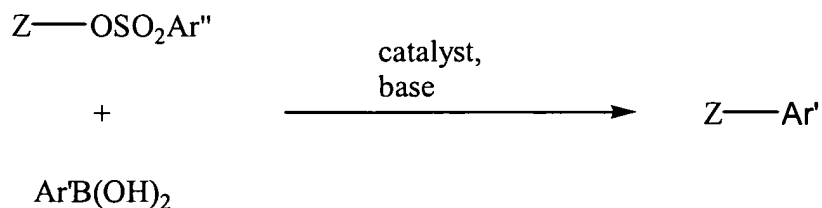
R_1 and R_2 , when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, halogen, $-SiR_3$, and $-(CH_2)_m-R_{80}$;

R_{80} represents independently for each occurrence cycloalkyl or aryl;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer.

40. The method of claim 39, wherein the transition metal is palladium.
41. The method of claim 39, wherein Z represents optionally substituted aryl.
42. A method represented by Scheme 4:



Scheme 4

wherein

Z and Ar' are independently selected from the group consisting of optionally substituted aryl, heteroaryl and alkenyl;

Ar'' is selected from the group consisting of optionally substituted aromatic moieties;

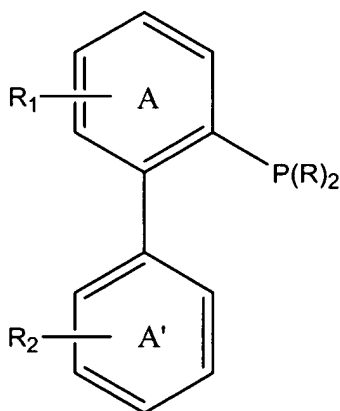
Z and Ar' may be covalently linked;

catalyst consists essentially of at least one palladium atom or ion; and at least one ligand;

the base is selected from the group consisting of fluorides, hydrides, hydroxides, carbonates, phosphates, alkoxides, metal amides, and carbanions; and

the ligand is selected from the group consisting of:

compounds represented by I:



I

wherein

R is selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and $-(CH_2)_m-R_{80}$;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R₁ and R₂, respectively, any number of times up to the limitations imposed by stability and the rules of valence;

R₁ and R₂, when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, -SiR₃,

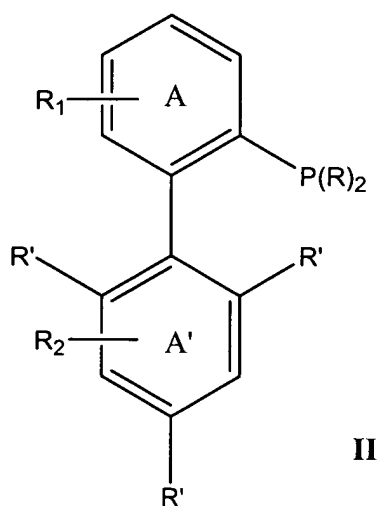
and $-(CH_2)_m-R_{80}$;

R_{80} represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer; and

compounds represented by **II**:



wherein

R and R' are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, and $-(CH_2)_m-R_{80}$;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R_1 and R_2 , respectively, any number of times up to the limitations imposed by stability and the rules of valence;

R_1 and R_2 , when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, halogen, $-SiR_3$, and $-(CH_2)_m-R_{80}$;

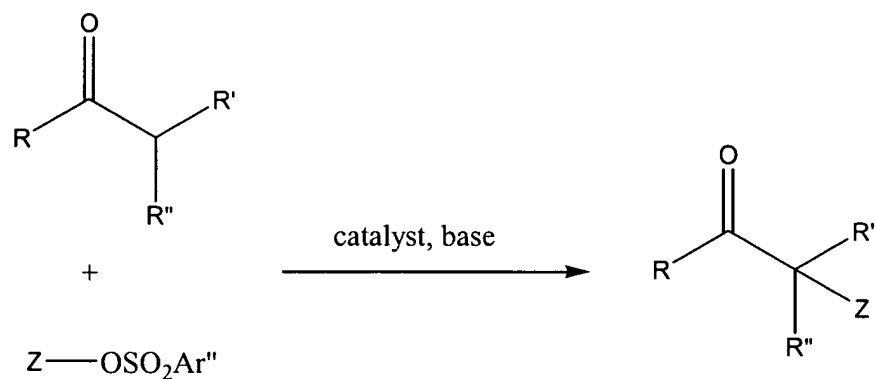
R_{80} represents independently for each occurrence cycloalkyl or aryl;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer.

43. The method of claim 42, wherein Z represents optionally substituted aryl.

44. The method of claim 42, wherein Ar'' is tolyl or phenyl.
45. The method of claim 42, wherein Ar'' is tolyl.
46. The method of claim 42, wherein the base is selected from the group consisting of fluorides, carbonates, and phosphates.
47. The method of claim 42, wherein the base is cesium fluoride, potassium fluoride, cesium carbonate, or potassium phosphate.
48. The method of claim 42, wherein Ar'' is tolyl or phenyl; and the base is selected from the group consisting of fluorides, carbonates, and phosphates.
49. The method of claim 42, wherein Ar'' is tolyl or phenyl; and the base is cesium fluoride, potassium fluoride, cesium carbonate, or potassium phosphate.
50. The method of claim 42, wherein Ar'' is tolyl; and the base is selected from the group consisting of fluorides, carbonates, and phosphates.
51. The method of claim 42, wherein Ar'' is tolyl; and the base is cesium fluoride, potassium fluoride, cesium carbonate, or potassium phosphate.
52. A method represented by Scheme 5:



Scheme 5

wherein

Z is selected from the group consisting of optionally substituted aryl, heteroaryl and alkenyl;

Ar'' is selected from the group consisting of optionally substituted aromatic moieties;

R is selected from the group consisting of H, alkyl, heteroalkyl, aralkyl, aryl, heteroaryl, alkoxyl, alkylthio, alkylamino, and arylamino;

R' is selected from the group consisting of H, alkyl, heteroalkyl, aralkyl, aryl, heteroaryl, formyl, acyl, alkoxycarbonyl, alkylaminocarbonyl, and arylaminocarbonyl;

R'' is selected from the group consisting of H, alkyl, heteroalkyl, aralkyl, aryl, and heteroaryl;

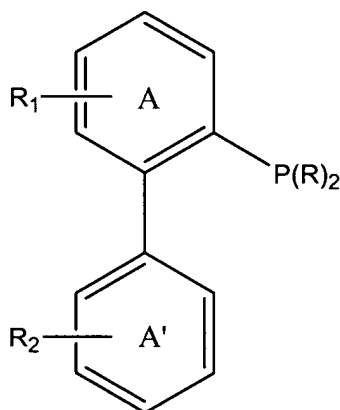
Z and one of R, R', and R'' may be covalently linked;

catalyst consists essentially of at least one palladium atom or ion; and at least one ligand;

the base is selected from the group consisting of fluorides, hydrides, hydroxides, carbonates, phosphates, alkoxides, metal amides, and carbanions; and

the ligand is selected from the group consisting of:

compounds represented by I:



I

wherein

R is selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and $-(CH_2)_m-R_{80}$;

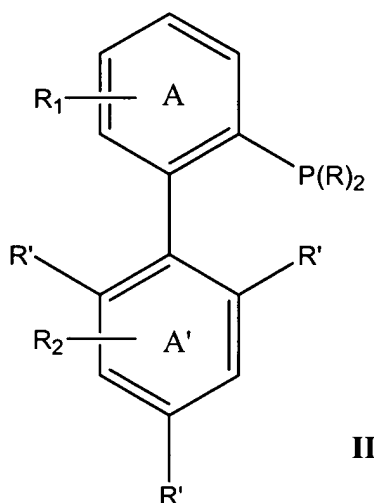
the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R₁ and R₂, respectively, any number of times up to the limitations imposed by stability and the rules of valence;

R_1 and R_2 , when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, $-\text{SiR}_3$, and $-(\text{CH}_2)_m\text{-R}_{80}$;

R_{80} represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer; and
compounds represented by **II**:



wherein

R and R' are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, and $-(\text{CH}_2)_m\text{-R}_{80}$;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R_1 and R_2 , respectively, any number of times up to the limitations imposed by stability and the rules of valence;

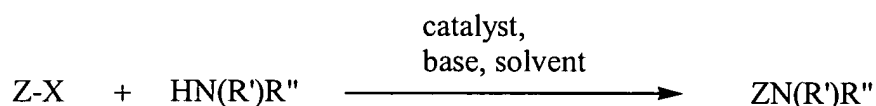
R_1 and R_2 , when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, halogen, $-\text{SiR}_3$, and $-(\text{CH}_2)_m\text{-R}_{80}$;

R_{80} represents independently for each occurrence cycloalkyl or aryl;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer.

53. The method of claim 52, wherein Z represents optionally substituted aryl.
54. The method of claim 52, wherein Ar'' is tolyl or phenyl.
55. The method of claim 52, wherein Ar'' is phenyl.
56. The method of claim 52, wherein the base is selected from the group consisting of fluorides, carbonates, and phosphates.
57. The method of claim 52, wherein the base is cesium fluoride, potassium fluoride, cesium carbonate, or potassium phosphate.
58. The method of claim 52, wherein Ar'' is tolyl or phenyl; and the base is selected from the group consisting of fluorides, carbonates, and phosphates.
59. The method of claim 52, wherein Ar'' is tolyl or phenyl; and the base is cesium fluoride, potassium fluoride, cesium carbonate, or potassium phosphate.
60. The method of claim 52, wherein Ar'' is phenyl; and the base is selected from the group consisting of fluorides, carbonates, and phosphates.
61. The method of claim 52, wherein Ar'' is phenyl; and the base is cesium fluoride, potassium fluoride, cesium carbonate, or potassium phosphate.
62. A method represented by Scheme 6:



Scheme 6

wherein

Z is selected from the group consisting of optionally substituted aryl, heteroaryl and alkenyl;

X is selected from the group consisting of Cl, Br, I, -OS(O)₂alkyl, and -OS(O)₂aryl;

R' and R'' are selected, independently for each occurrence, from the group consisting of H, alkyl, heteroalkyl, aryl, formyl, acyl, alkoxycarbonyl, alkylaminocarbonyl, heteroaryl, aralkyl, alkoxy, amino, trialkylsilyl, and triarylsilyl;

R' and R'', taken together, may form an optionally substituted ring consisting of 3-10 backbone atoms inclusive; said ring optionally comprising one or more heteroatoms beyond the nitrogen to which R' and R'' are bonded;

R' and/or R'' may be covalently linked to Z;

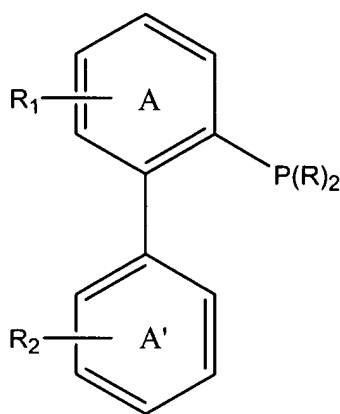
solvent is water;

catalyst consists essentially of at least one palladium atom or ion; and at least one ligand;

the base is selected from the group consisting of fluorides, hydroxides, carbonates, phosphates, and alkoxides; and

the ligand is selected from the group consisting of:

compounds represented by I:



I

wherein

R is selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and $-(CH_2)_m-R_{80}$;

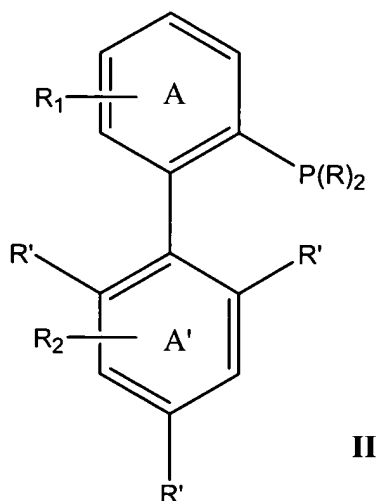
the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R_1 and R_2 , respectively, any number of times up to the limitations imposed by stability and the rules of valence;

R_1 and R_2 , when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, $-\text{SiR}_3$, and $-(\text{CH}_2)_m\text{-R}_{80}$;

R_{80} represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer; and compounds represented by **II**:



wherein

R and R' are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, and $-(\text{CH}_2)_m\text{-R}_{80}$;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R_1 and R_2 , respectively, any number of times up to the limitations imposed by stability and the rules of valence;

R_1 and R_2 , when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, halogen, $-\text{SiR}_3$, and $-(\text{CH}_2)_m\text{-R}_{80}$;

R₈₀ represents independently for each occurrence cycloalkyl or aryl;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and
the ligand, when chiral, is a mixture of enantiomers or a single enantiomer.

63. The method of claim 62, wherein the base is selected from the group consisting of carbonates and hydroxides.

64. The method of claim 62, wherein the base is selected from the group consisting of sodium carbonate, potassium carbonate, cesium carbonate, sodium hydroxide and potassium hydroxide.

65. The method of claim 62, wherein the base is selected from the group consisting of potassium carbonate, sodium hydroxide and potassium hydroxide.

66. The method of claim 62, wherein X is Cl, Br or I.

67. The method of claim 62, wherein X is Cl or Br.

68. The method of claim 62, wherein X is Cl.

69. The method of claim 62, wherein Z represents optionally substituted aryl.

70. The method of claim 62, wherein Z is optionally substituted phenyl.

71. The method of claim 62, wherein the base is selected from the group consisting of carbonates and hydroxides; and X is Cl, Br or I.

72. The method of claim 62, wherein the base is selected from the group consisting of carbonates and hydroxides; X is Cl, Br or I; and Z is optionally substituted phenyl.

73. The method of claim 62, wherein the base is selected from the group consisting of carbonates and hydroxides; and X is Cl or Br.

74. The method of claim 62, wherein the base is selected from the group consisting of carbonates and hydroxides; X is Cl or Br; and Z is optionally substituted phenyl.

75. The method of claim 62, wherein the base is selected from the group consisting of carbonates and hydroxides; and X is Cl.

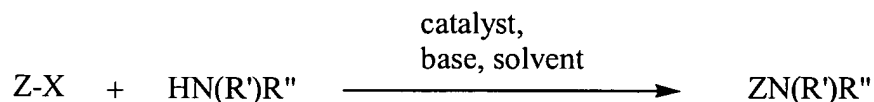
76. The method of claim 62, wherein the base is selected from the group consisting of carbonates and hydroxides; X is Cl; and Z is optionally substituted phenyl.

77. The method of claim 62, wherein the base is selected from the group consisting of potassium carbonate, sodium hydroxide, and potassium hydroxide; X is Cl, Br, or I; and Z is optionally substituted phenyl.

78. The method of claim 62, wherein the base is selected from the group consisting of potassium carbonate, sodium hydroxide, and potassium hydroxide; X is Cl or Br; and Z is optionally substituted phenyl.

79. The method of claim 62, wherein the base is selected from the group consisting of potassium carbonate, sodium hydroxide, and potassium hydroxide; X is Cl; and Z is optionally substituted phenyl.

80. A method represented by Scheme 7:



Scheme 7

wherein

Z is selected from the group consisting of optionally substituted aryl, heteroaryl and alkenyl;

X is selected from the group consisting of Cl, Br, I, -OS(O)₂alkyl, and -OS(O)₂aryl;

R' and R'' are selected, independently for each occurrence, from the group consisting of H, alkyl, heteroalkyl, aryl, formyl, acyl, alkoxycarbonyl, alkylaminocarbonyl, heteroaryl, aralkyl, alkoxyl, amino, trialkylsilyl, and triarylsilyl;

R' and R'', taken together, may form an optionally substituted ring consisting of 3-10 backbone atoms inclusive; said ring optionally comprising one or more heteroatoms beyond the nitrogen to which R' and R'' are bonded;

R' and/or R'' may be covalently linked to Z;

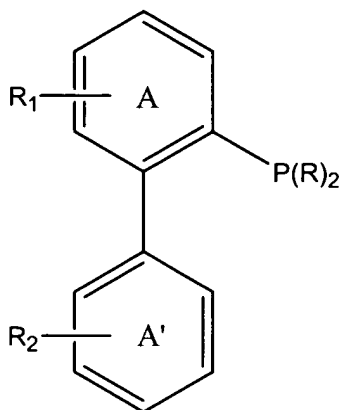
catalyst consists essentially of at least one palladium atom or ion; and at least one ligand;

solvent comprises a hydroxylic solvent in greater than 50% by volume;

the base is selected from the group consisting of fluorides, hydroxides, carbonates, phosphates, and alkoxides; and

the ligand is selected from the group consisting of:

compounds represented by **I**:



I

wherein

R is selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and $-(CH_2)_m-R_{80}$;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R_1 and R_2 , respectively, any number of times up to the limitations imposed by stability and the rules of valence;

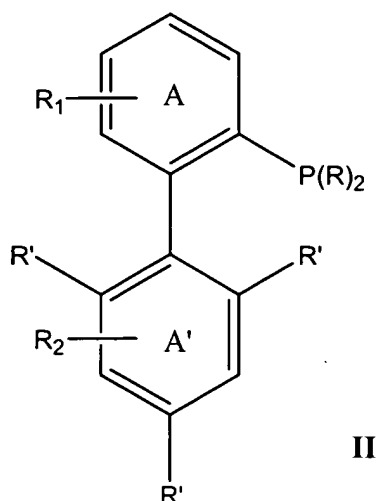
R_1 and R_2 , when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, $-SiR_3$, and $-(CH_2)_m-R_{80}$;

R_{80} represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer; and

compounds represented by **II**:



wherein

R and R' are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, and $-(CH_2)_m-R_{80}$;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R₁ and R₂, respectively, any number of times up to the limitations imposed by stability and the rules of valence;

R₁ and R₂, when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, halogen, $-SiR_3$, and $-(CH_2)_m-R_{80}$;

R₈₀ represents independently for each occurrence cycloalkyl or aryl;

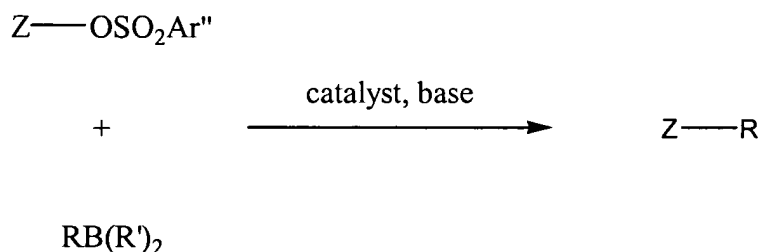
m is independently for each occurrence an integer in the range 0 to 8 inclusive; and the ligand, when chiral, is a mixture of enantiomers or a single enantiomer.

81. The method of claim 80, wherein said hydroxylic solvent is a lower alkyl alcohol.
82. The method of claim 80, wherein said hydroxylic solvent is tert-butanol.
83. The method of claim 80, wherein said solvent consists essentially of said hydroxylic solvent.
84. The method of claim 80, wherein the base is selected from the group consisting of alkoxides, carbonates, phosphates and hydroxides.

85. The method of claim 80, wherein the base is selected from the group consisting of sodium phosphate, potassium phosphate, sodium tert-butoxide, potassium tert-butoxide, sodium carbonate, potassium carbonate, sodium hydroxide and potassium hydroxide.
86. The method of claim 80, wherein X is Cl or Br.
87. The method of claim 80, wherein Z represents optionally substituted aryl.
88. The method of claim 80, wherein Z is optionally substituted phenyl.
89. The method of claim 80, wherein said hydroxylic solvent is a lower alkyl alcohol; and said solvent consists essentially of said hydroxylic solvent.
90. The method of claim 80, wherein said hydroxylic solvent is tert-butanol; and said solvent consists essentially of said hydroxylic solvent.
91. The method of claim 80, wherein said hydroxylic solvent is a lower alkyl alcohol; said solvent consists essentially of said hydroxylic solvent; and the base is selected from the group consisting of alkoxides, carbonates, phosphates and hydroxides.
92. The method of claim 80, wherein said hydroxylic solvent is a lower alkyl alcohol; said solvent consists essentially of said hydroxylic solvent; the base is selected from the group consisting of alkoxides, carbonates, phosphates and hydroxides; and X is Cl or Br.
93. The method of claim 80, wherein said hydroxylic solvent is a lower alkyl alcohol; said solvent consists essentially of said hydroxylic solvent; the base is selected from the group consisting of alkoxides, carbonates, phosphates and hydroxides; X is Cl or Br; and Z is optionally substituted phenyl.
94. The method of claim 80, wherein said hydroxylic solvent is tert-butanol; said solvent consists essentially of said hydroxylic solvent; and the base is selected from the group consisting of sodium phosphate, potassium phosphate, sodium tert-butoxide, potassium tert-butoxide, sodium carbonate, potassium carbonate, sodium hydroxide and potassium hydroxide.
95. The method of claim 80, wherein said hydroxylic solvent is tert-butanol; said solvent consists essentially of said hydroxylic solvent; the base is selected from the group consisting of sodium phosphate, potassium phosphate, sodium tert-butoxide, potassium tert-butoxide, sodium carbonate, potassium carbonate, sodium hydroxide and potassium hydroxide; and X is Cl or Br.

96. The method of claim 80, wherein said hydroxylic solvent is tert-butanol; said solvent consists essentially of said hydroxylic solvent; the base is selected from the group consisting of sodium phosphate, potassium phosphate, sodium tert-butoxide, potassium tert-butoxide, sodium carbonate, potassium carbonate, sodium hydroxide and potassium hydroxide; X is Cl or Br; and Z is optionally substituted phenyl.

97. A method represented by Scheme 8:



Scheme 8

wherein

Z is selected from the group consisting of optionally substituted aryl, heteroaryl and alkenyl;

Ar'' is selected from the group consisting of optionally substituted aromatic moieties;

R is selected from the group consisting of optionally substituted alkyl and aralkyl;

R' is selected, independently for each occurrence, from the group consisting of alkyl and heteroalkyl; the carbon-boron bond of said alkyl and heteroalkyl groups being inert under the reaction conditions; B(R')₂ taken together may represent 9-borobicyclo[3.3.1]nonyl.

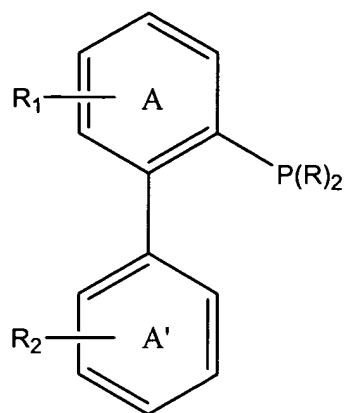
Z and R may be covalently linked;

catalyst consists essentially of at least one palladium atom or ion; and at least one ligand;

the base is selected from the group consisting of fluorides, hydrides, hydroxides, carbonates, phosphates, alkoxides, metal amides, and carbanions; and

the ligand is selected from the group consisting of:

compounds represented by I:



wherein

R is selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and $-(CH_2)_m-R_{80}$;

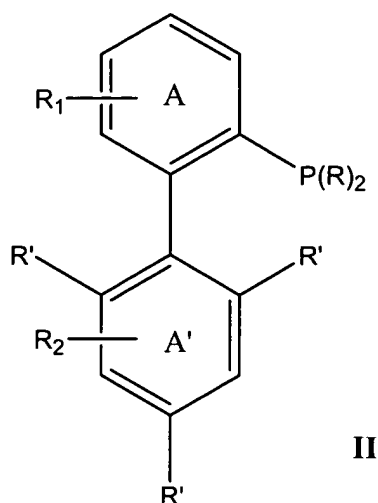
the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R_1 and R_2 , respectively, any number of times up to the limitations imposed by stability and the rules of valence;

R_1 and R_2 , when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, $-SiR_3$, and $-(CH_2)_m-R_{80}$;

R_{80} represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, is a mixture of enantiomers or a single enantiomer; and
compounds represented by II:



wherein

R and R' are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, and $-(CH_2)_m-R_{80}$;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R₁ and R₂, respectively, any number of times up to the limitations imposed by stability and the rules of valence;

R₁ and R₂, when present, are selected independently for each occurrence from the group consisting of alkyl, cycloalkyl, halogen, $-SiR_3$, and $-(CH_2)_m-R_{80}$;

R₈₀ represents independently for each occurrence cycloalkyl or aryl;

m is independently for each occurrence an integer in the range 0 to 8 inclusive; and
the ligand, when chiral, is a mixture of enantiomers or a single enantiomer.

98. The method of claim 97, wherein Z represents optionally substituted aryl.

99. The method of claim 97, wherein Ar'' is tolyl or phenyl.

100. The method of claim 97, wherein the base is selected from the group consisting of fluorides, carbonates, and phosphates.

101. The method of claim 97, wherein the base is cesium fluoride, potassium fluoride, cesium carbonate, or potassium phosphate.

102. The method of claim 97, wherein $B(R')_2$ taken together represents 9-borobicyclo[3.3.1]nonyl.

103. The method of claim 97, wherein Ar'' is tolyl or phenyl; and the base is selected from the group consisting of fluorides, carbonates, and phosphates.

104. The method of claim 97, wherein Ar'' is tolyl or phenyl; and the base is cesium fluoride, potassium fluoride, cesium carbonate, or potassium phosphate.

105. The method of claim 97, wherein Ar'' is tolyl or phenyl; the base is selected from the group consisting of fluorides, carbonates, and phosphates; and $B(R')_2$ taken together represents 9-borobicyclo[3.3.1]nonyl.

106. The method of claim 97, wherein Ar'' is tolyl or phenyl; the base is cesium fluoride, potassium fluoride, cesium carbonate, or potassium phosphate; and $B(R')_2$ taken together represents 9-borobicyclo[3.3.1]nonyl.